Renewable and Sustainable Energy Reviews 37 (2014) 90–99

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

# Recent patent issues on intermediate reflectors for high efficiency thin-film silicon photovoltaic devices

Seung Yeop Myong *

*Energy R&D Center, KISCO, Miamri 1044, Jeungpyeong-eup, Jeungpyeong-gun, Choongcheongbuk-do 368-906, Republic of Korea*

ARTICLE INFO

*Article history:*
Received 9 March 2013
Received in revised form
23 April 2014
Accepted 3 May 2014
Available online 27 May 2014

*Keywords:*
Thin-film silicon photovoltaic device
Intermediate reflector
Light trapping
Metal oxide
Silicon alloy
Series integration

ABSTRACT

The recent surge of unveiled US patents on the intermediate reflectors for thin-film silicon (Si) photovoltaic (PV) devices reflects the paramount importance of light trapping to improve the conversion efficiency. Here, the recent patent issues on the intermediate reflectors of thin-film Si PV devices are reviewed. Highly transparent and conductive metal oxide intermediate reflectors have the advantage of the higher efficiency for the fabricated multi-junction solar cells compared to the Si alloy intermediate reflectors. However, their high lateral electrical conductivity leads to the lateral shunting during the monolithic series integration of segments. To avoid the lateral shunt creations, an additional laser scribe or a coating process that induces a high production cost is necessary. In addition, a low conversion efficiency for hydrogenated amorphous silicon (a-Si:H)/hydrogenated microcrystalline Si (μc-Si:H) double-junction PV modules employing a metal oxide intermediate reflector stems from the decrease in the active area as a result of the additional process. Meanwhile, double-junction PV modules employing an n-type hydrogenated microcrystalline Si oxide (n-μc-$SiO_x$:H) intermediate reflector provide a higher conversion efficiency. Since the Si alloy intermediate reflector can avoid the lateral shunting, it may be a promising option for cost-effective mass production of large-area thin-film Si multi-junction PV modules. Although the developed intermediate reflectors have the high potential, the current status is limited at the research and development (R&D) level. Therefore, the up-scaling with the low cost, high throughput, and high yield is a key technological mission for mass production.



**Contents**

1. Introduction . . . 90
2. Device concept and the survey for related patents . . . 91
   2.1. Concept of the related technology . . . 91
   2.2. Search method for related patents . . . 92
3. Patent issues and discussion . . . 93
   3.1. Metal oxide intermediate reflectors . . . 93
   3.2. Si alloy intermediate reflectors . . . 94
   3.3. Other intermediate reflectors . . . 95
   3.4. Series integration considering intermediate reflectors . . . 95
   3.5. Discussion . . . 96
4. Conclusion . . . 97
References . . . 97

## 1. Introduction

It is known that recent global warming caused by excess emission of $CO_2$ warns that the climate change and nuclear power plants are no longer stable and cheap energy source after Fukushima nuclear meltdowns. Sufficient supplies of clean energy are

* Tel.: +82 43 8389146; fax: +82 43 8389144.
*E-mail address:* myongsy@kaist.ac.kr

http://dx.doi.org/10.1016/j.rser.2014.05.016
1364-0321/

intimately linked with global stability, economic prosperity, and quality of life. Accordingly, clean renewable energy including solar, wind, and hydrogen energy becomes a prime issue. A photovoltaic (PV) module using solar light is a promising candidate among the renewable energy sources because the sun is our primary source of clean, abundant energy. Actually, there has been an explosive, worldwide increase in the PV module market during the last two decades. However, the oversupply of bulk crystalline silicon (c-Si) PV modules that currently shares 80% of products and the decrease in government subsidies due to the recent global economic crisis threat the PV business by causing the rapid drop in the module price. The thin-film silicon (Si) PV modules using hydrogenated amorphous Si (a-Si:H) and/or hydrogenated microcrystalline Si (μc-Si:H) absorbers have been considered as promising alternatives to the bulk c-Si PV modules due to the various advantages of remarkably low consumption of the raw Si material ( $<1\%$ of consumption of bulk c-Si PV modules), large-area deposition, low-temperature production, and low temperature coefficient. The thin-film Si PV technology also profits from the wide experience base of display industries [1]. However, the recent sharp drop in the module price gives rise to a need for a new breakthrough in the conversion efficiency ($\eta$) as well as the cost of the thin-film Si PV modules.

However, the so-called "Staebler–Wronski effect (SWE)" in a-Si:H-based films remains as a major technical challenge for the commercialization of the thin-film Si PV modules [2,3]. SWE is the light-induced degradation arising from the photocreation of dangling bonds accomplished by nonradiative recombination of photogenerated electron–hole pairs [4]. To reduce SWE in a-Si:H absorbers that leads to the degradation of thin-film Si solar cells, there have been extensive investigations during the past 30 years. As a result, stabilized $\eta$ ($\eta_{sta}$) about 10% has been reported for a-Si:H single-junction solar cells [5]. However, reported highest $\eta_{sta}$ of research and development (R&D)-level a-Si:H single-junction PV modules is 8.7% [6] and that of single-junction PV module products is 6–7% [5]. Double-junction solar cells composed of a-Si:H top and the μc-Si:H bottom cells stacked in series have been developed to achieve a high value of $\eta_{sta}$ by guiding incident light to the appropriate absorbers [7–10]. Because the μc-Si:H bottom cell is very stable against red light irradiation [11], the reduced thickness of the a-Si:H absorber in the top cell compared to that of a-Si:H absorbers in conventional single-junction solar cells provides a good stability against light soaking. To date, $\eta_{sta}$ of 10–11% has been reported for R&D-level a-Si:H/μc-Si:H double-junction PV modules, while $\eta_{sta}$ of 9–10% has been achieved for a-Si:H/μc-Si:H double-junction PV module products [12]. The stability of the a-Si:H/μc-Si:H double-junction solar cells mainly depends on the light-induced degradation as well as the thickness of the absorber in the top cell. Thus, improved light trapping in the a-Si:H top cell using an intermediate reflector becomes the center of R&D interest.

A lower refractive index ($n$) of an intermediate reflector compared to $n$ of Si layers ($\sim$4.0) is essential in enhancing the internal reflection [13]. It was reported that highly conductive and transparent zinc oxide (ZnO) intermediate reflectors having $n$ of $\sim$2.0 significantly increased $\eta_{sta}$ of superstrate-type a-Si:H/μc-Si:H double-junction solar cells [14,15]. Despite the improvement of the cell performances, however, the metal oxide intermediate reflector including ZnO is not suitable for mass production of superstrate type thin-film Si PV modules due to the lateral shunting [16] caused by the leakage current path generation between the intermediate reflector and metal back contact. To prevent a poor fill factor (FF) as a result of the monolithic series integration, at least an additional step is required for the isolation of the exposed intermediate reflector after the laser scribe of Si layers from the subsequently coated metal back contact. This additional step gives rise to a high production cost. In the case of substrate-type a-Si:H/μc-Si:H double-junction solar cells, improved light trapping by employing a textured ZnO intermediate reflector was also reported [17]. However, the substrate-type a-Si:H/μc-Si:H double-junction PV modules employing the textured ZnO intermediate reflector also suffer from a similar lateral shunting. A leakage current path occurs between the highly conductive ZnO intermediate reflector and subsequently prepared transparent front electrode like indium tin oxide (ITO) and ZnO.

Alternatively, hydrogenated n-type amorphous silicon-oxide (n-a-$SiO_x$:H) and hydrogenated n-type microcrystalline (or nanocrystalline) silicon-oxide (n-μc-$SiO_x$:H) intermediate reflectors with a constant $n$ value were developed [18–22]. The $SiO_x$:H intermediate reflectors can considerably reduce the lateral shunting due to the lower lateral conductivity than the ZnO intermediate reflectors. Also, the $SiO_x$:H intermediate reflectors can be removed simultaneously with adjacent Si layers via the laser scribe of Si layers. Hence, no additional step for the monolithic integration of a-Si:H/μc-Si:H double-junction PV modules is necessary. Moreover, the *in situ* preparation of $SiO_x$:H intermediate reflectors using plasma enhanced chemical vapor deposition (PECVD) is possible. Due to the key technological issue of improved light trapping for thin-film Si PV devices, considerable inventions focused on the intermediate reflector are timely published as patents. In this work, the author will review the recent trends of patents on the intermediate reflectors of thin-film Si PV modules.

## 2. Device concept and the survey for related patents

### 2.1. Concept of the related technology

Fig. 1 shows the images of installed thin-film Si PV modules by the Korean module manufacturer, KISCO. The thin-film Si PV modules can be used variously as terrestrial modules in the outdoor field, building applied photovoltaic (BAPV) modules, and building integrated photovoltaic (BIPV) modules.

Fig. 2 exhibits the structure of a superstrate-type a-Si:H/μc-Si:H double-junction PV module. 1.1 m $\times$ 1.3 m-sized (so-called "Gen5") glasses are widely used as substrates. The front transparent conductive oxide (TCO) is coated on a side of the glass substrate as a front electrode. The p–i–n type a-Si:H top cell and μc-Si:H bottom cell structures are deposited on the front electrode by the PECVD techniques using a mixture of $SiH_4$-based reactant gases. An intermediate reflector with a low $n$ value is inserted between the top and bottom cells. After the deposition of Si thin films, the back reflector and metal back contacts are subsequently formed. The monolithic series integration of the double-junction PV modules was materialized via the plurality of three parallel laser-scribed patterns (P1–P3 patterns). The Q-switched infrared (IR) laser with the wavelength of 1064 nm or ultraviolet (UV) laser is used for P1 patterns depending on the front electrode materials. The Q-switched green laser with the wavelength of 532 nm is used for P2 and P3 patterns. Finally, the module encapsulation is performed by laminating the back sheet including an Al foil or a back cover glass with an ethylene–vinyl acetate (EVA) film. Incident solar light transmitting the front TCO-coated glass is absorbed in the i-a-Si:H and i-μc-Si:H layers and thus electron–hole pairs are created. The photocreated carriers are drifted to the respective electrodes by the electric field formed in the absorbers. The electrons are collected by the metal back contacts and the holes are collected by the transparent front electrodes. The intermediate reflector plays an important role in reflecting penetrated visible light to the top cell and transmitting near-IR light to the bottom cell. For the effective internal reflection, the refractive index difference ($\Delta n$) between the intermediate reflector and neighboring Si layer is an important design factor together with the thickness of the intermediate reflector. The high transmittance and reduced thickness are essential for the low optical absorption loss in the intermediate

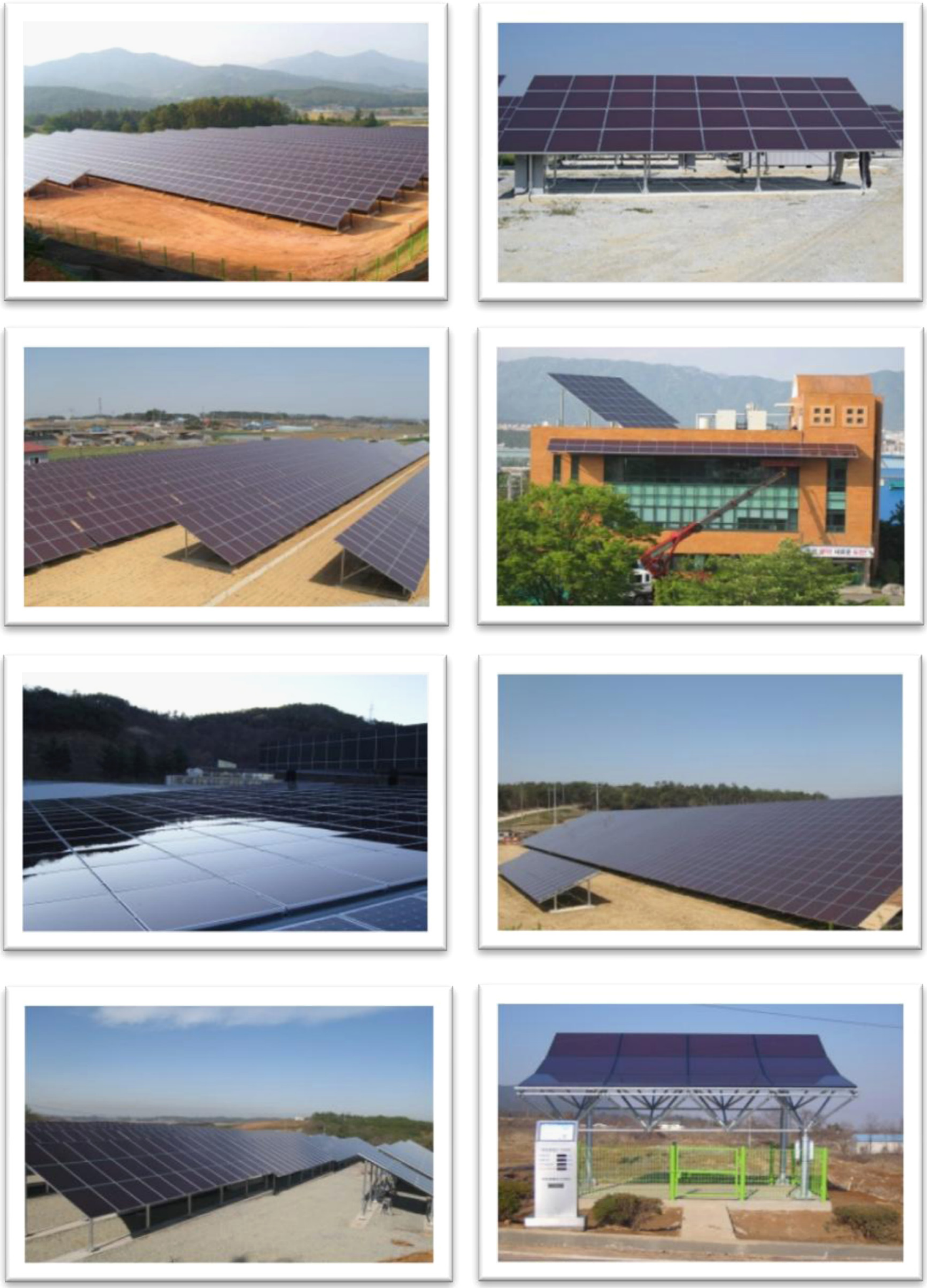


**Fig. 1.** Thin-film Si PV modules deployed by KISCO.

reflector. The high vertical electrical conductivity of the intermediate reflector is also required not to increase the electrical loss.

### *2.2. Search method for related patents*

The legally valid United States (US) patents have been surveyed because the US patents are regarded as the international patents. The author started the survey from 0.1 million patents of $>600$ institutions using an online patent search service named “WIPS” with the first keywords of “solar or photovoltaic or photoelectric.” Then, a lot of noise was filtered using the detailed keywords of “semiconductor or device or method or apparatus or battery or module or panel or converter or system or cell or element or film.” Related patents were finally selected through author's in-depth

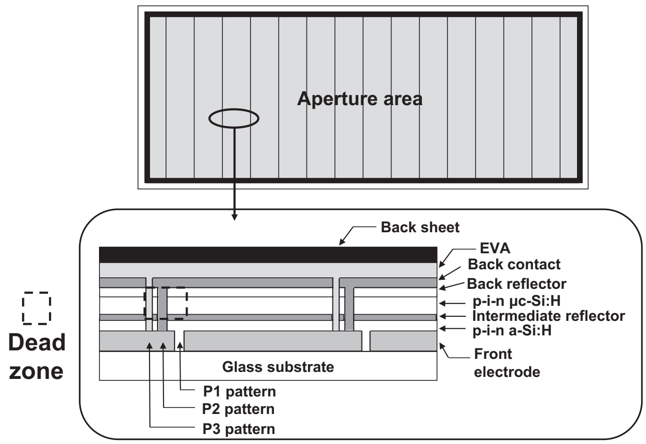



**Fig. 2.** Planar and cross-sectional views for the structure of the superstrate-type a-Si:H/μc-Si:H double-junction PV module with an intermediate reflector.

**Table 1**
Top 12 assignees for the US patents on the intermediate reflectors for thin-film Si PV devices.

| Rank | Assignee | Total publications |
|---|---|---|
| 1 | KISCO | 16 |
| 2 | Sanyo Electric | 15 |
| 3 | MHI | 11 |
| 4 | Sharp | 7 |
| 4 | Samsung Electronics | 7 |
| 6 | Kaneka | 6 |
| 7 | LG Electronics | 4 |
| 8 | Applied Materials | 3 |
| 8 | IMT, EPFL | 3 |
| 8 | Mitsubishi Electric | 3 |
| 8 | Nexpower Technology | 3 |
| 8 | TEL Solar | 3 |

analysis of claims. As a result, 92 published and registered patents claimed the intermediate reflectors of thin-film Si PV modules have been selected for this review.

## 3. Patent issues and discussion

Table 1 provides the list of top 12 assignees for the US patents on the intermediate reflectors of thin-film Si PV devices. The Korean module manufacturer with the brand name of "GETWATT", KISCO, takes the first place by disclosing 16 patents related to effective *n* grading of Si alloy intermediate reflectors [23–38]. The Japanese company, Sanyo Electric, takes the second place with the various 15 patents [39–53]. The Japanese module manufacturer, Mitsubishi Heavy Industry (MHI), takes the third place with the 11 patents related to sputter ZnO intermediate reflectors [54–64]. The Japanese module manufacturer, Sharp, published 7 patents which focused on the textured ZnO and silicon nitride ($SiN_x$) intermediate reflectors [65–71]. The Korean company, Samsung Electronics, also published 7 patents based on recent R&D [72–78]. The Japanese module manufacturer, KANEKA, invented 6 patents leading R&D of thin-film Si PV modules [79–84]. The Korean company, LG Electronics, has 4 patents based on R&D and pilot module production [85–88]. The global vacuum equipment supplier, Applied Materials (AMAT), invented 3 patents based on the various material attempts to develop intermediate reflectors [89–91]. IMT, EPFL, is a Swiss research group that firstly developed a-Si:H/μc-Si:H double-junction solar cells and invented the concept of the intermediate reflector [14]. This group has 3 published patents related to the surface texture configuration of the intermediate reflector [92–94]. The Japanese company, Mitsubishi Electric [95–97] and Taiwanese module manufacturer, Nexpower Technology [98–100], also disclose 3 related inventions each. The Swiss company, Oerlikon Solar, was recently merged into the Japanese turnkey solution supplier for mass production of thin-film Si PV modules, TEL Solar. It is also possessing 3 published patents [100–102]. Fig. 3 displays the annual number of filed patents on the intermediate reflectors of thin-film Si PV devices. After the first patent emerged in 2000, the number increased gradually in the early 2000s. The boom for filed patents was ignited in 2008 and the number reached the sharp peak value of 21 in 2009. This tendency reveals the recent paramount interest in the intermediate reflectors of the thin-film Si PV technology. There are relatively diminished numbers from 2011 because patents filed in these years are currently publishing.

The surveyed 92 patents were classified according to the detailed technology – metal oxide intermediate reflectors, Si alloy intermediate reflectors, and series integration of modules considering a conductive metal oxide intermediate reflector. As shown in Fig. 4, the patents classified to the metal oxide intermediate reflectors, Si alloy intermediate reflectors, and series integration technology share 27.2%, 33.7%, and 31.5%, respectively. Hereafter, the author will review the classified patents.

### 3.1. Metal oxide intermediate reflectors

Highly transparent and conductive metal oxide films have been widely used as the intermediate reflectors of thin-film Si double-junction solar cells. As a single layer intermediate reflector, various

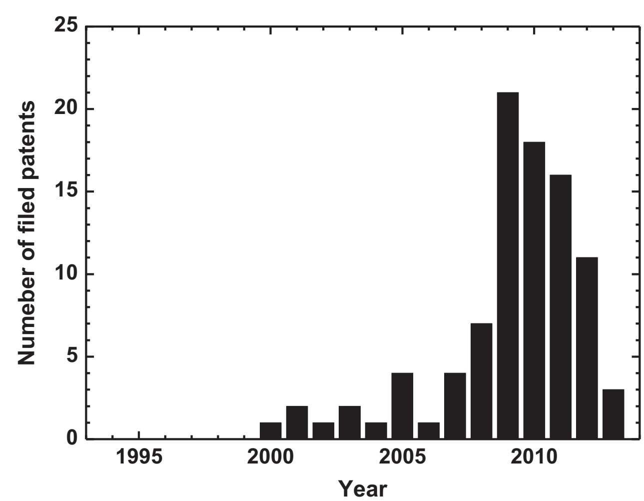



**Fig. 3.** The annual number of filed US patents regarding on intermediate reflectors of thin-film Si PV modules.

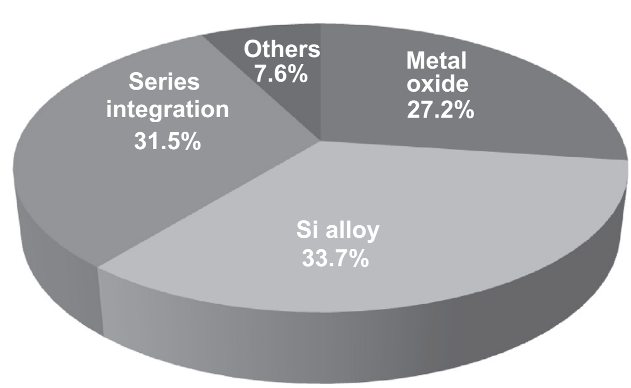



**Fig. 4.** The distribution of major classification for the reviewed patents on intermediate reflectors of thin-film Si PV modules.

TCO materials have been disclosed. ZnO, tin oxide ($SnO_2$), and ITO intermediate reflectors were introduced in refs. [54,55]. Especially, a bottom cell-limited current matching configuration was claimed for thin-film Si double-junction solar cells employing the intermediate reflectors in ref. [56]. Also, ZnO, $SnO_2$, ITO and indium oxide ($In_2O_3$) intermediate reflectors were introduced in ref. [104]. In ref. [105], various metal oxide materials such as ZnO, Ga-doped ZnO (ZnO:Ga), ITO, Al-doped ZnO (ZnO:Al), indium zinc oxide (IZO), indium tin zinc oxide (ITZO), aluminum tin oxide (ATO), cadmium indium oxide (CIO), cadmium zinc oxide (CZO), and F-doped $SnO_2$ ($SnO_2$:F) were claimed for intermediate reflectors. In addition, a Nb-doped titanium dioxide ($TiO_2$:Nb) intermediate reflector was developed [89]. The structural combination of the ZnO:Al intermediate reflector and n-μc-$SiO_x$:H/ZnO:Al back reflector was proposed in ref. [85]. The surface-textured, metal oxide intermediate reflectors were claimed in refs. [92,93]. The textured surface can scatter light properly and thus reinforce light trapping by increasing the optical path length inside the solar cells. A textured ZnO intermediate reflector was disclosed in ref. [66]. The sputter-etched ZnO intermediate reflector can be prepared by chemical wet etching for the surface of sputter ZnO using an acid solution [64,66]. In particular, an asymmetric ZnO intermediate reflector was developed for high efficiency substrate-type a-Si:H/μc-Si:H double-junction solar cells with a n–i–p configuration [94]. The CVD ZnO film prepared by low pressure CVD (LPCVD) [107–109] or metal–organic CVD (MOCVD) [110] is suitable for the asymmetric ZnO intermediate reflector because the pyramidal rough surface can be naturally formed under the growth conditions for the $(11-20)$ preferential crystallographic orientation. In addition, undoped ZnO or lightly B-doped ZnO (ZnO:B) is favorable as the asymmetric intermediate reflector because the excess B doping of CVD ZnO causes an adverse effect that reduces the surface roughness and enhances the free carrier absorption in the near-IR range [109]. In ref. [72], porous ZnO, ITO, $SnO_2$, and $In_2O_3$ were proposed as intermediate reflectors. Again, their nanostructures such as nanorods, nanotubes, and nanowires were proposed as the intermediate reflectors. In ref. [97], a metal oxide intermediate reflector including micropores filled with metals was invented to enhance the vertical electrical conductivity. In ref. [44], the thickness control of a metal oxide intermediate reflector depending on the crystallinity of the i-μc-Si:H absorber in the bottom cell was proposed.

To improve the electrical, optical and structural properties, considerable bilayer metal oxide intermediate reflectors were disclosed. In ref. [39], a low $n$ metal oxide (ZnO or ITO)/contact layer (ZnO or $In_2O_3$) bilayer was developed to improve the interface between the intermediate reflector and p-μc-Si:H window layer of the bottom cell. In ref. [69], an undoped ZnO/amorphous buffer bilayer intermediate reflector was invented to improve the interface. In ref. [68], the structure of the undoped ZnO with a higher hydrogen content/undoped ZnO with a lower hydrogen content obtained using a $H_2$ plasma treatment was proposed as the intermediate reflector. Effective light trapping may be attained using the layers having different $n$ values. In ref. [40], zinc magnesium oxide ($ZnMg_xO$)/ZnO and $ZnMg_xO/In_2O_3$ bilayers were claimed as intermediate reflectors. The Mg content leads to the lower $n$ value and higher resistivity compared to ZnO. In ref. [58], ZnO:Ga/$ZnMg_xO$ and $ZnMg_xO$ with a lower Mg content/$ZnMg_xO$ bilayers were developed to avoid the lateral shunting of the metal oxide intermediate reflectors. Alternatively, a $H_2$ plasma-treated ZnO-based bilayer was developed in ref. [59] to solve the problem. The first layer may be ZnO:Ga, Ga and N-codoped ZnO (ZnO:Ga:N), or Ga and N-codoped $ZnMg_xO$ ($ZnMg_xO$:Ga:N), while the second layer may be ZnO:Ga:N or $ZnMg_xO$:Ga:N. In ref. [95], an n-type metal oxide (ZnO, ITO, $SnO_2$, IZO or indium gallium zinc oxide (InGaZnO))/p-type metal oxide (NiO, $Cu_2O$, or $ZnM_2O_4$ (M=Co, Rh, or Ir)) bilayer intermediate reflector was developed.

For further optimization of light trapping, trilayer and alternated multilayer stack were also disclosed as intermediate reflectors. In ref. [60], a ZnO:Ga/$TiO_2$/ZnO:Ga trilayer was proposed as a intermediate reflector. In ref. [61], an alternated multilayer stack comprised of ZnO and plasma-resistant protecting Si alloy ($SiO_x$ or silicon-oxycarbide ($SiO_xC_y$)) sublayers was introduced to prevent the reduction of ZnO during the deposition of the p-μc-Si:H window layer of the bottom cell. In ref. [79], an alternated multilayer stack consisting of carbon sublayers and ZnO sublayers was introduced. In ref. [111], alternated multilayer intermediate reflectors comprised of oxide, nitride, ITO, ZnO, or $SnO_2$ were disclosed.

On the other hand, the structural combination of the ZnO:Al intermediate reflector and n-μc-$SiO_x$:H/ZnO:Al back reflector was proposed in ref. [85]. Intermediate reflectors aiming for improved light trapping of triple-junction solar cells were also disclosed. In ref. [56], the structure of top cell/the first textured ZnO:Ga intermediate reflector/middle cell/the second textured ZnO:Ga intermediate reflector/bottom cell was claimed. The textured ZnO:Ga intermediate reflectors have the sine-curved surface texture. In ref. [57], the structure of a-Si:H top cell/the first ZnO:Ga intermediate reflector/μc-Si:H middle cell/the second ZnO:Ga intermediate reflector/μc-SiGe:H bottom cell was developed. In ref. [112], the substrate-type triple-junction solar cell with the structure of a-Si:H top cell/a-Si:H middle cell/metal oxide intermediate reflector/μc-Si:H bottom cell was invented.

### 3.2. Si alloy intermediate reflectors

Despite the metal oxide intermediate reflectors led to high $\eta$ of the thin-film Si multi-junction solar cells; however, their high lateral electrical conductivity induced the lateral shunting. Thus, various Si alloy intermediate reflectors have been disclosed. The $n$ reducing elements such as O, C, and N can effectively adjust $n$ of the intermediate reflector in the range of 1.7–3.6. However, the vertical electrical conductivity decreases as the content of the $n$ reducing elements increases. Therefore, a compromise between the vertical electrical conductivity and $n$ is necessary for the design of the Si alloy intermediate reflectors. As single layer intermediate reflectors, $SiO_x$, $SiN_x$, silicon-carbide ($SiC_x$), $SiO_xC_y$, silicon-oxynitride ($SiO_xN_y$), and silicon-carbon-nitride ($SiC_xN_y$) films were claimed in ref. [106]. In refs. [102,113], a $SiO_x$:H intermediate reflector was claimed. In refs. [90,101], a μc-$SiO_x$:H intermediate reflector was developed. In ref. [80], n-μc-$SiO_x$:H and n-a-$SiO_x$:H intermediate reflectors were developed. In ref. [114], an n-$SiO_x$:H intermediate reflector with very low $n$ ($<1.7$) was claimed. The structural combination of the n-μc-$SiO_x$:H intermediate reflector and n-μc-$SiO_x$:H/ZnO:Al back reflector was proposed in ref. [85]. In ref. [70], a $SiN_x$:H intermediate reflector with openings was demonstrated to enhance the vertical electrical conductivity. Effective $n$ grading of the Si alloy intermediate reflectors could increase the internal reflection. In ref. [41], a graded n-μc-$SiO_x$:H intermediate reflector from a high $n$ value to a low $n$ value was proposed. More various graded n-μc-$SiO_x$:H intermediate reflectors using gradual or stepwise O grading method were developed in refs. [23,24,34]. Similarly, various graded n-μc-$SiC_x$:H and n-μc-$SiN_x$:H intermediate reflectors were developed in refs. [25,27]. In ref. [26], graded n-μc-$SiO_x$:H, n-μc-$SiC_x$:H, and n-μc-$SiN_x$:H intermediate reflectors using a roll-to-roll process were developed for flexible thin-film Si PV modules. In order to reinforce light trapping by increasing the optical path length inside the solar cells, the surface-textured intermediate reflectors were claimed in refs. [92,93]. In ref. [97], the $SiO_x$ intermediate reflector including the micropores filled with metals was invented to enhance the vertical electrical conductivity. In ref. [44], the thickness control of a $SiO_x$ intermediate reflector

depending on the crystallinity of the i-μc-Si:H absorber in the bottom cell was proposed.

Effective $n$ grading can be materialized using bilayer intermediate reflectors. In ref. [73], $SiO_x$, $SiN_x$, and $SiC_x$ bilayers having the first layer with higher $n$ and second layer with lower $n$ were disclosed as intermediate reflectors. In ref. [91], n-μc-$SiO_x$:H/n-μc-Si:H, n-μc-$SiC_x$:H/n-μc-Si:H, and n-μc-$SiN_x$:H/n-μc-Si:H bilayer intermediate reflectors were proposed to improve the fill factor (FF) of the multi-junction solar cells by compensating the vertical electrical conductivity. In ref. [81], n-a-$SiO_x$:H/p-a-$SiO_x$:H bilayer was developed to act as the intermediate reflector and tunnel junction simultaneously. In ref. [43], a μc-Si:H bottom cell including a graded p-$SiO_x$:H (low $n$ to high $n$) window layer and graded n-$SiO_x$:H (high $n$ to low $n$) layer was demonstrated.

As a trilayer intermediate reflector, the structure of i-μc-Si:H/n-a-$SiO_x$:H/i-μc-Si:H and doped μc-Si:H/n-a-$SiO_x$:H/doped μc-Si:H was disclosed in ref. [42]. To optimize the thickness and internal multiple reflection, various alternated multilayer stacks were disclosed as intermediate reflectors. An alternated multilayers comprised of n-μc-Si:H and n-μc-Si:H alloy (n-μc-$SiO_x$:H, n-μc-$SiC_x$:H, or n-μc-$SiN_x$:H) sublayers were invented as intermediate reflectors [28–30,33]. In ref. [79], an alternated multilayer stack comprised of carbon and $SiO_x$ sublayers was developed. In ref. [115], an alternated multilayer stack comprised of Si alloy ($SiO_x$, $SiC_x$, or $SiN_x$) and n-type Si (n-a-Si:H or n-μc-Si:H) sublayers were developed. In ref. [111], an alternated multilayer intermediate reflectors made of $SiC_x$ were disclosed. The reflectance ($R$) of the alternated multilayer reflectors can be simply estimated by the following equation:

$$R = [(n_R^{2i} - 1)/(n_R^{2i} + 1)]^2 \quad (1)$$

where $n_R$ is the refractive index ratio of the sublayer with higher $n$ over the sublayer with lower $n$ and $i$ is the number of total stacking cycles [116]. With the $n_R$ value of 1.8, the two-cycled alternated multilayer intermediate reflector has $R$ of 0.682, whereas the three-cycled alternated multilayer intermediate reflector has higher $R$ of 0.889. Thus, the alternated multilayer is a promising option as the intermediate reflector.

Si alloy intermediate reflectors for improved light trapping of triple-junction solar cells were also disclosed. In ref. [82], the structure of a-Si:H top cell/a-Si:H middle cell/n-a-$SiO_x$:H or n-μc-$SiO_x$:H intermediate reflector/μc-Si:H bottom cell was claimed. In ref. [112], the substrate type triple-junction solar cell with the structure of a-Si:H top cell/a-Si:H middle cell/Si alloy intermediate reflector/μc-Si:H bottom cell was developed.

### 3.3. Other intermediate reflectors

In ref. [46], an amorphous carbon (a-C:H) intermediate reflector was disclosed. In ref. [100], opaque intermediate reflectors made of graphite or a metal with openings were developed. The opaque intermediate reflectors were connected to a reflection enhancing bilayer consisting of high $n$ and low $n$ layers. In ref. [38], a metal nanoparticle intermediate reflector was developed. The metallic nanoparticles such as Au and Ag can reflect visible light into the top cell and deliver reinforced near-IR light into the bottom cell due to the surface plasmon resonance [117]. In metallic nanoparticles, localized plasmons corresponding to collective oscillations of conduction electrons within the particle rather than traveling waves on the surface can be excited. The metallic nanoparticles then act as "antenna" for incident light by enhancing field intensities in the vicinity of localized plasmons [118–122]. The metallic nanoparticles could be embedded in the Si alloy and metal oxide films to enhance the internal reflection. To obtain very low $n$ (1.0–2.0) of intermediate reflectors, metal or mixed alloy nanoparticles were embedded in a transparent binder material in refs [123,124]. In ref. [87], the triple-junction solar cell structure of a-$SiO_x$:H or a-$SiC_x$:H top cell/the first intermediate reflector with $n_1$/a-SiGe:H middle cell/the second intermediate reflector with $n_2$/μc-SiGe:H bottom cell was developed. The intermediate reflectors have different $n$ values in the specific wavelength ranges.

### 3.4. Series integration considering intermediate reflectors

In general, a-Si:H/μc-Si:H double-junction PV modules employing the Si alloy intermediate reflector are monolithically series-connected by the plurality of the three laser patterns (see Fig. 2). However, the a-Si:H/μc-Si:H double-junction PV modules employing the metal oxide intermediate reflector require an additional process to avoid the later shunting that originates from the high lateral electrical conductivity. In refs. [45,46], the monolithic series integration was realized only by two laser patterning processes because of the additional insulator and conductor coatings. As plotted in Fig. 5a, the intermediate reflector is patterned together with the top cell, bottom cell, and metal back contact by the P2 laser scribe.

In ref. [86], the conventional monolithic series integration (see Fig. 2) was used despite the conductive intermediate reflector.

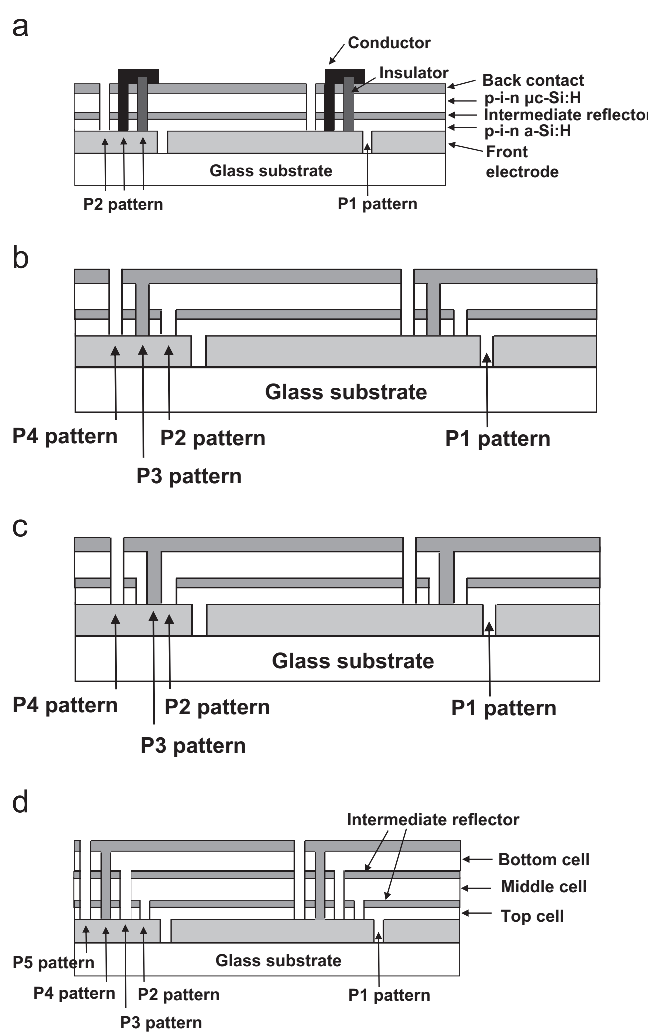



**Fig. 5.** Cross-sectional images of the series integration of thin-film Si PV modules considering conductive metal oxide intermediate reflectors comprised of (a) combination of two laser-scribed patterns and coatings of the insulator and conductor (ref. [45]); (b) typical four laser-scribed patterns (ref. [84]), (c) four laser-scribed patterns including the overlapped P2 and P3 patterns (ref. [71]); and (d) five laser-scribed patterns for the triple-junction structure (ref. [87]).

However, considerable lateral shuntings are expected. If an additional process is executed to reduce the lateral shunting, the monolithic series integration can be materialized by the plurality of the three laser patterns as shown in Fig. 2. In ref. [47], the intermediate reflector was patterned together with the bottom cell by the P2 laser illuminated from the metal back contact side and then exposed side walls were etched by reactive plasma. Subsequently, the insulator and conductor coatings were performed to complete the series integration. In ref. [48], the intermediate reflector was patterned together with the top and bottom cells by the P2 laser scribe and polymer compound coatings were followed at the exposed side walls. In ref. [49], the intermediate reflector was patterned together with the top and bottom cells by the P2 laser scribe; however the lateral shunting can be reduced by increasing the Schottky barrier [109] between the metal back contact and intermediate reflector at the exposed side walls. In ref. [50], the lateral shunting could be reduced by forming a p–n tunnel junction at end sections of the intermediate reflector via an additional doping. In ref. [74], the lateral shunting could be inhibited using the conductive intermediate reflector with openings. The intermediate reflector was patterned together with the top and bottom cells by the P2 laser scribe. In ref. [75], the lateral shunting could be avoided by positioning the insulating spacer at the end sections of the intermediate reflector. Also, the intermediate reflector was patterned together with the top and bottom cells by the P2 laser scribe. In refs. [98,99], the lateral shunting could be avoided by depositing an isolated intermediate reflector using a mask. To maximize the active area of double-junction thin-film Si PV modules, various point contact techniques were invented. The electrical connection between neighboring segments could be materialized through point contacts (through holes) by contacting the front electrode of a cell to the back contact of a neighboring cell. In refs. [35,36], the intermediate reflector was patterned together with the top and bottom cells as the forms of the through holes by the P2 laser scribe. To prevent the lateral shunting, a high resistive layer was formed by oxidizing the exposed sidewall of the through holes using a physical or a chemical method in ref. [35], while an insulated layer was coated on the exposed sidewall of the through holes in ref. [36]. The trenches formed by the P1 and P3 laser scribes could be overlapped except near the point contacts. Besides, the trenches formed a closed loop surrounding a point contact.

The monolithic series integration of the a-Si:H/μc-Si:H double-junction PV modules can be realized by the plurality of four laser patterns. Fig. 5b depicts the typical structure introduced in ref. [84]. The intermediate reflector was patterned together with the top cell by the P2 laser scribe, and the P2 and P3 patterns were separated. Fig. 5c reveals an alternative structure claimed in ref. [71]. The intermediate reflector was patterned together with the top cell by the P2 laser scribe, and the P2 and P3 patterns were overlapped. Other alternative structures were also disclosed [46,51,53,78]. In ref. [76], the intermediate reflector was patterned together with the top and bottom cells by the P3 laser scribe. In refs. [77,125], the intermediate reflector was patterned solely by the P2 laser scribe. In refs. [62–64], the intermediate reflector was patterned together with a portion of the top cell by the P2 laser scribe. Especially, an a-Si:H recrystallized region was formed beneath the P2 patterns in order to perfectly prevent the lateral shunting in ref. [64]. In ref. [52], the intermediate reflector was patterned together with the top cell, bottom cell, and metal back contact by the P2 laser scribe and the monolithic series integration was completed by a subsequent conductor and insulator coatings. In ref. [37], the intermediate reflector was patterned together with the top cell as the form of through holes by the P2 laser scribe. To prevent the lateral shunting, the bottom cell deposited inside the through holes formed by the P2 laser scribe was patterned as the form of point contacts (inner through holes) using the P3 laser scribe. Alternatively, the bottom cell could be patterned together with the top cell and intermediate reflector as the form of point contacts (through holes) using the P3 laser scribe beside the through holes formed by the P2 laser scribe. The trenches formed by the P1 and P4 laser scribes could be overlapped except near the point contacts. Also, the trenches formed a closed loop surrounding a point contact formed by the P3 laser scribe and a through hole formed by the P2 laser scribe. In ref. [97], the intermediate reflector was patterned together with the top and bottom cells by the P2 laser scribe. To avoid the lateral shunting, the trench formed by the P2 laser scribe was filled with white, dielectric reflection pigments.

In addition, the monolithic series integration for triple-junction modules was disclosed using the plurality of five laser patterns. As shown in Fig. 5d, the first intermediate reflector was patterned together with the top cell by the P2 laser scribe, and the second intermediate reflector was patterned together with the top and middle cells by the P3 laser scribe (in ref. [87]). In ref. [83], the hybrid triple-junction structure of top cell/intermediate reflector/middle cell/compound thin-film bottom cell was developed. The intermediate reflector was patterned solely by the P2 laser scribe.

### 3.5. Discussion

Table 2 describes the record performances of thin-film Si PV devices employing intermediate reflectors reported in the reviewed patents. MHI reported the highest initial $\eta$ value ($\eta_{ini}$) of 13.2% for a-Si:H/μc-Si:H double-junction solar cells by adopting the ZnO:Ga intermediate reflector prepared by sputtering [55]. MHI also reported $\eta_{sta}$ of 11.8% for the same structure [57]. Kaneka achieved highest $\eta_{ini}$ of 12.9% for the a-Si:H/μc-Si:H double-junction solar cells by employing the n-μc-$SiO_x$:H intermediate reflector [80], whereas TEL Solar achieved $\eta_{ini}$ of 13.1% and $\eta_{sta}$ of 11.8% for the same structure [103]. Meanwhile, Sharp obtained $\eta_{ini}$ of 12.6% for the a-Si:H/μc-Si:H double-junction solar cells using the $SiN_x$:H intermediate reflector [70]. For a-Si:H/μc-Si:H/μc-SiGe:H triple-junction solar cells, MHI recorded highest $\eta_{ini}$ of 15.1% by employing the sputter ZnO:Ga intermediate reflectors [57]. Kaneka achieved $\eta_{ini}$ of 13.5% by employing the n-a-$SiO_x$:H intermediate reflectors for a-Si:H/a-Si:H/μc-Si:H triple-junction solar cells [82], while Sharp achieved $\eta_{ini}$ of 13.8% by employing the $SiN_x$:H intermediate reflectors for the same triple-junction structure [70]. In the case of a-Si:H/μc-Si:H double-junction mini-modules, Sanyo obtained $\eta_{ini}$ of 11.6% by employing the sputter ZnO:Al intermediate reflector [53]. Besides, Kaneka obtained highest $\eta_{ini}$ of 13.2% by employing the n-μc-$SiO_x$:H intermediate reflector [80]. It is found that the ZnO-based metal oxide intermediate reflectors lead to higher $\eta_{ini}$ values for both double-junction and triple-junction solar cells than the various Si alloy intermediate reflectors. However, the trend of $\eta_{ini}$ is reversed for the monolithically series-connected double-junction modules. It is inferred that the highly conductive ZnO-based metal oxide intermediate reflectors cause a significant lateral shunting as a result of the series integration of the neighboring segments. Therefore, numbers of patents were involved to solve the lateral shunting. In addition, many of the patents were focusing on effective $n$ grading in order to improve the internal reflection and reduce the optical loss in the intermediate reflector. Recently, state-of-the-art n-$SiO_x$:H-based intermediate reflectors for superstrate type a-Si:H/μc-Si:H double-junction solar cells have been reported. Using the n-μc-$SiO_x$:H intermediate reflector with $n$ of 1.85, $\eta_{ini}$ of 12.3% and $\eta_{sta}$ of 11.1% was achieved [126]. The structural combination of the n-μc-$SiO_x$:H intermediate reflector and n-μc-$SiO_x$:H/Ag back reflector was also reported [127]. In addition, high $\eta_{ini}$ of 13.1% and $\eta_{sta}$ of 11.5% were achieved for a-Si:H/μc-Si:H double-junction solar cells by employing the alternated multilayer intermediate reflector comprised of

**Table 2**
Record performances for the thin-film Si multi-junction PV devices reported by US patents.

| Type | Cell structure | Intermediate reflector | Assignee | $\eta_{ini}$ (%) | $\eta_{sta}$ (%) | Reference |
|---|---|---|---|---|---|---|
| Cell | a-Si:H/μc-Si:H | Sputter ZnO:Ga | MHI | 12.5 | 11.8 | Ref. [55] |
| | a-Si:H/μc-Si:H | Sputter ZnO:Ga | MHI | 13.2 | – | Ref. [57] |
| | a-Si:H/μc-Si:H | Sputter-etched ZnO:Ga | Sharp | 12.6 | – | Ref. [66] |
| | a-Si:H/μc-Si:H substrate-type | LPCVD ZnO | EPFL | – | 9.8 | Ref. [93] |
| | a-Si:H/μc-Si:H | n-μc-$SiO_x$:H | TEL Solar | 13.1 | 11.8 | Ref. [103] |
| | a-Si:H/μc-Si:H | n-μc-$SiO_x$:H | Kaneka | 12.9 | – | Ref. [80] |
| | a-Si:H/μc-Si:H | n-μc-$SiO_x$:H | EPFL | 12.1 | – | Ref. [92] |
| | a-Si:H/μc-Si:H | n-μc-$SiO_x$:H | Samsung | 11.7 | – | Ref. [73] |
| | a-Si:H/μc-Si:H | n-μc-$SiO_x$:H | LG | 11.6 | – | Ref. [85] |
| | a-Si:H/μc-Si:H | $SiO_x$:H | United Solar | 11.0 | 10.3 | Ref. [114] |
| | a-Si:H/μc-Si:H | $SiN_x$:H | Sharp | 12.6 | – | Ref. [70] |
| | a-Si:H/μc-Si:H/μc-SiGe:H | Sputter ZnO:Ga | MHI | 15.1 | – | Ref. [57] |
| | a-Si:H/a-Si:H/μc-Si:H | n-μc-$SiO_x$:H | Kaneka | 13.0 | – | Ref. [82] |
| | a-Si:H/a-Si:H/μc-Si:H | n-a-$SiO_x$:H | Kaneka | 13.5 | – | Ref. [82] |
| | a-Si:H/a-Si:H/μc-Si:H | $SiN_x$:H | Sharp | 13.8 | – | Ref. [70] |
| Module | a-Si:H/μc-Si:H | Sputter ZnO:Al | Sanyo | 11.6 | – | Ref. [53] |
| | a-Si:H/μc-Si:H | Sputter ZnO:Al:Ga | Kaneka | 11.5 | – | Ref. [84] |
| | a-Si:H/μc-Si:H | n-μc-$SiO_x$:H | Kaneka | 13.2 | – | Ref. [80] |

n-a-Si:H and n-a-$SiO_x$:H sublayers [128]. In order to inhibit the creation of nanocracks in the i-μc-Si:H bottom cell absorber, the concept of the smoothened intermediate reflector by coating a highly transparent and insulating UV-curable lacquer ($n=1.5$) on the textured ZnO layer prepared by LPCVD was proposed [129]. 3-Dimensional (3D) photonic crystal intermediate reflectors were reported for effective light trapping in the a-Si:H/μc-Si:H double-junction solar cells [130–132]. To obtain a low $n$ value, a conductive 3D photonic crystal intermediate reflector was materialized via the inversed ZnO opals, which are fabricated by ZnO-replication of polymeric opals using CVD or atomic layer deposition (ALD) techniques. In the case of substrate type a-Si:H/μc-Si:H double-junction solar cells, improved light trapping by employing a textured ZnO intermediate reflector was also reported [133]. As a result, $\eta_{ini}$ of 11.2% and $\eta_{sta}$ of 9.8% were obtained. On the other hand, state-of-the-art n-$SiO_x$:H-based intermediate reflectors for triple-junction solar cells have been recently reported. In the case of superstrate type a-Si:H/a-SiGe:H/μc-Si:H triple-junction solar cells, high $\eta_{ini}$ of 16.1% was obtained by inserting a n-μc-$SiO_x$:H intermediate reflector between the middle and bottom cells [134,135]. By optimizing the same structure with the substrate type configuration, highest $\eta_{ini}$ of 16.3% and $\eta_{sta}$ of 13.6% were achieved [136,137]. The reported high $\eta$ values of thin-film Si multi-junction solar cells verify the high potential of the intermediate reflector technology for effective light trapping. However, all the reported results have been limited at the small-sized R&D level. Therefore, the up-scaling with the low cost, high throughput, and high yield is a key technological mission for mass production of high efficiency thin-film Si multi-junction PV modules employing the intermediate reflectors.

## 4. Conclusion

The author has reviewed the recent trends of US patents on the intermediate reflectors for thin-film Si PV devices. The highly transparent and conductive metal oxide intermediate reflectors have the advantage of higher $\eta$ for the fabricated double-junction and triple-junction solar cells compared to the Si alloy intermediate reflectors. However, the lateral shunting of monolithically series-connected modules occurs due to the high lateral electrical conductivity. To avoid the lateral shunting, the additional process that elevates the production cost and inactive area is necessary. Thus, the relatively lower $\eta$ value for the fabricated a-Si:H/μc-Si:H double-junction modules were reported compared to that for the fabricated a-Si:H/μc-Si:H double-junction modules employing the n-μc-$SiO_x$:H intermediate reflector. Since the Si alloy intermediate reflector can avoid the lateral shunting problem during the monolithic series integration of segments, it is a promising option for cost-effective mass production of large-area thin-film Si multi-junction PV modules. Even though the developed intermediate reflectors have a high potential, the related PV activities are currently limited at the R&D level. Therefore, the up-scaling with low cost, high throughput, and high yield is a key technological mission for mass production. This review will help the researchers and engineers interested in the thin-film Si PV technology by providing the disclosed materials for the intermediate reflectors, strategies for the effective internal reflection, and the monolithic series integration to avoid the lateral shunting. Although inventions of innovative intermediate reflectors are still in progress, the related patents published from May, 2014, are not included in this review.

## References

[1] Shah A, Torres P, Tscharner R, Wyrsch N, Keppner H. Photovoltaic technology: the case for thin-film solar cells. Science 1999;285:692–8.
[2] Kazmerski LL. Photovoltaics: a review of cell and module technologies. Renew Sustain Energy Rev 1997;1:71–170.
[3] Zein NE, Lamont LA, Chaar LE. Review of photovoltaic technologies. Renew Sustain Energy Rev 2011;15:2165–75.
[4] Staebler DL, Wronski CR. Reversible conductivity changes in discharge-produced amorphous Si. Appl Phys Lett 1997;31:292–4.
[5] Konagai M. Present status and future prospects of silicon thin-film solar cells. Jpn J Appl Phys 2011;50 (Article ID 030001. 12 pp.).
[6] Fecioru-Morariu M, Mereu B, Bakehe S, Kalas J, Kluth O, Eisenhammer T. High quality amorphous Si solar cells for large area mass production Micromorph tandem cells. J Non-Cryst Solids 2012;358:2264–7.
[7] Meier J, Vallat-Sauvain E, Dubail S, Kroll U, Dubail J, Golay S, et al. Microcrystalline/micromorph silicon thin-film solar cells prepared by VHF-CD technique. Sol Energy Mater Sol Cells 2001;66:73–84.
[8] Yamamoto K, Yoshimi M, Tawada Y, Okamoto Y, Nakajima A. Thin film Si solar cell fabricated at low temperature. J Non-Cryst Solids 2000;266–269:1082–7.
[9] Rech B, Kluth O, Repmann T, Roschek T, Springer J, Müller J, et al. New materials and deposition techniques for highly efficient silicon thin film solar cells. Sol Energy Mater Sol Cells 2002;74:439–47.
[10] Yan B, Yue G, Yang J, Guha S, Williamson DL, Han D, et al. Light-induced metastability in hydrogenated nanocrystalline silicon solar cells. Appl Phys Lett 2004;85:1955–7.
[11] Gordijn A, Rath JK, Schropp REI. High-efficiency μc-Si solar cells made by very high-frequency plasma-enhanced chemical vapor deposition. Prog Photovolt: Res Appl 2006;14:305–11.

[12] Klein S, Rohde M, Buschbaum S, Severin D. Throughput optimized a-Si/μc-Si:H tandem solar cells on sputter-etched ZnO substrates. Sol Energy Mater Sol Cells 2012;98:363–9.
[13] Krc J, Brecl K, Smole F, Topic M. The effects of enhanced light trapping in tandem micromorph silicon solar cells. Sol Energy Mater Sol Cells 2006;90:3339–44.
[14] Dominé D, Bailat J, Steinhauser J, Shah A, Ballif C. Micromorph solar cell optimization using a ZnO layer as intermediate reflector. In: Proceedings of the conference records of 2006 IEEE 4th world conference on photovoltaic energy conversion, Hawaii, USA; 2006, p. 1465–8.
[15] Myong SY, Sriprapha K, Miyajima S, Konagai M, Yamada A. High efficiency protocrystalline silicon/microcrystalline silicon tandem cell with zinc oxide intermediate layer. Appl Phys Lett 2007;90 (Article ID 263509. 3 pp.).
[16] Meillaud F, Feltrin A, Dominé D, Buehlmann P, Python M, Bugnon G, et al. Limiting factors in the fabrication of microcrystalline silicon solar cells and microcrystalline/amorphous ('micromorph') tandems. Philos Mag 2009;89:2599–621.
[17] Soderstrom T, Haug F-J, Terrazzoni-Daudrix V, Ballif C. Flexible micromorph tandem a-Si/μc-Si solar cells. J Appl Phys 2010;107 (Article ID 014507. 7 pp.).
[18] Yamamoto K, Nakajima A, Yoshimi M, Sawada T, Fukuda S, Suezaki T, et al. A thin-film silicon solar cell and module. Prog Photovolt: Res Appl 2005;13:489–94.
[19] Buehlmann P, Bailat J, Dominé D, Billet A, Meillaud F, Feltrin A, et al. In situ silicon oxide based intermediate reflector for thin-film silicon micromorph solar cells. Appl Phys Lett 2007;91 (Article ID 143505. 3 pp.).
[20] Das C, Lambertz A, Huepkes J, Reetz W, Finger F. A constructive combination of antireflection and intermediate-reflector layers for a-Si/μc-Si:H thin film solar cells. Appl Phys Lett 2008;92 (Article ID 053509. 3 pp.).
[21] Veneri PD, Mercaldo LV, Usatii I. Improved micromorph solar cells by means of mixed-phase n-doped silicon oxide layers. Prog Photovolt: Res Appl 2013;21:148–55.
[22] Lambertz A, Grundler T, Finger F. Hydrogenated amorphous silicon oxide containing a microcrystalline silicon phase as an intermediate reflector in thin-film silicon solar cells. J Appl Phys 2011;109 (Article ID 113109. 10 pp.).
[23] Myong S-Y. Tandem thin-film silicon solar cell and method for manufacturing the same. United States patent 2014, 8648251; February 11.
[24] Myong S-Y. Tandem thin-film silicon solar cell and method for manufacturing the same. United States patent 2014, 8628995; January 14.
[25] Myong S-Y. Photovoltaic device and method for manufacturing the same. United States patent application publication 2011, 2011/0048499; March 3.
[26] Myong S-Y. Photovoltaic device including an inflexible or a flexible substrate and method for manufacturing the same. United States patent 2014, 8642373; February 4.
[27] Myong S-Y. Photovoltaic device and method for manufacturing the same. United States patent application publication 2012, 2012/0325303; December 27.
[28] Myong S-Y. Photovoltaic device and method for manufacturing the same. United States patent application publication 2011, 2011/0061716; March 17.
[29] Myong S-Y. Photovoltaic device and method for manufacturing the same. United States patent 2014, 8669465; March 11.
[30] Myong SY. Photovoltaic device including flexible or inflexible substrate and method for manufacturing the same. United States patent application publication 2012, 2012/0073636; March 29.
[31] Myong S-Y. Photovoltaic device including flexible or inflexible substrate and method for manufacturing the same. United States patent 2013, 8502065; August 6.
[32] Myong S-Y. Photovoltaic device and method for manufacturing the same. United States Patent application publication 2011, 2011/0056538; March 10.
[33] Myong S-Y. Method for manufacturing photovoltaic device including flexible or inflexible substrate. United States patent 2013, 8426240; April 23.
[34] Myong S-Y, Jeon L-S. Thin film type solar cells and manufacturing method thereof. United States patent application publication 2013, 2013/0167917; July 4.
[35] Jeon L-S, Myong S-Y. Tandem type integrated photovoltaic module and manufacturing method thereof. United States patent application publication 2013, 2013/0206216; August 15.
[36] Myong S-Y, Jeon L-S. Integrated thin film photovoltaic module and manufacturing method thereof. United States patent application publication 2013, 2013/0312815; November 28.
[37] Jeon L-S, Myong S-Y. Tandem type integrated photovoltaic module and manufacturing method thereof. United States Patent application publication 2013, 2013/0312816; November 28.
[38] Myong SY. Photovoltaic device including flexible substrate or inflexible substrate and method for manufacturing the same. United States patent application publication 2013, 2013/0340818; December 26.
[39] Yata S. Solar cell. United States patent application publication 2012, 2012/0138126; June 7.
[40] Sekimoto T, Yata S, Saita A. Solar cell. United States patent application publication 2010, 2010/0282297; November 11.
[41] Sekimoto T, Yata S, Matsumoto M. Solar cell and manufacturing method thereof. United States patent application publication 2012, 2012/0305053; December 6.
[42] Yata S. Solar cell. United States patent application publication 2012, 2012/0305062; December 6.
[43] Yamaoka Y, Yata S. Photoelectric conversion device. United States patent application publication 2013, 2013/0014810; January 17.
[44] Yata S. Photoelectric conversion device. United States patent application publication 2013, 2013/0000710; January 3.
[45] Shinohara W. Photovoltaic apparatus and method of manufacturing the same. United States patent 2012, 8207441; June 26.
[46] Shinohara W. Solar cell module. United States patent application publication 2012, 2012/0138131; June 7.
[47] Shinohara W. Photovoltaic cell, photovoltaic cell module, method of fabricating photovoltaic cell and method of repairing photovoltaic cell. United States patent 2009, 7638707; December 29.
[48] Shinohara W. Solar cell module. United States patent application publication 2010, 2010/0300517; December 2.
[49] Sekimoto T, Yata S. Photovoltaic device and manufacturing method thereof. United States patent application publication 2010, 2010/0139751; June 10.
[50] Kunii T, Yata S. Photovoltaic device and manufacturing method for a photovoltaic device. United States patent application publication 2011, 2011/0197952; August 18.
[51] Shinohara W. Photovoltaic apparatus. United States patent 2012, 8115094; February 14.
[52] Shinohara W. Photovoltaic and method of manufacturing the same. United States patent 2013, 8362354; January 29.
[53] Murata K, Matsumoto M. Solar cell module and method of manufacturing the same. United States patent application publication 2009, 2009/0165840; July 2.
[54] Nakano Y, Yamashita N. Tandem thin film solar cell. United States patent application publication 2006, 2006/0086385; April 27.
[55] Nakano Y, Yamashita N. Thin-film solar cell of tandem type. United States patent application publication 2006, 2006/0086386; April 27.
[56] Kobayashi Y, Sakai S, Goya S. Photovoltaic device. United States patent application publication 2011, 2011/0126903; June 2.
[57] Goya S, Kobayashi Y, Sakai S. Photovoltaic device. United States patent application publication 2012, 2012/0012168; January 19.
[58] Yamaguchi K, Sakai S, Tsuruga S. Photoelectric conversion device. United States patent 2013, 8598447; December 3.
[59] Yamaguchi K, Yamashita N. Photovoltaic device. United States patent application publication 2012, 2012/0090664; April 19.
[60] Sakai S, Kobayashi Y. United States patent application publication 2012, 2012/0006402; January 12.
[61] Kobayashi Y, Sakai S, Yamaguchi K, Asahara Y, Goya S. Photovoltaic device and process for producing same. United States patent application publication 2010, 2010/0116331; May 13.
[62] Nishimiya T, Uda K, Kawazoe K, Baba T, Ishide T. Photoelectric conversion device fabrication method and photoelectric conversion device. United States patent application publication 2011, 2011/0126894; June 2.
[63] Uda K, Baba T, Ishide T, Kawazoe K, Nishimiya T. Photoelectric conversion device fabrication method and photoelectric conversion device. United States patent application publication 2011, 2011/0126895; June 2.
[64] Kawazoe K, Uda K, Baba T, Ishide T, Nakao S. Method for manufacturing photoelectric-conversion device, device for photoelectric-conversion-device manufacturing device, and photoelectric conversion device. United States patent application publication 2011, 2011/0226748; September 22.
[65] Muramoto M, Hayakawa T. Multi-junction solar cell. United States patent 2004, 6787692; September 7.
[66] Wada K, Nasuno Y, Kondo M, Matsuda A. Solar cell substrate, thin-film solar cell, and multi-junction thin-film solar cell. United States patent 2002, 6459034, October 1.
[67] Nagano Y, Koide N, Nakano T, Yang M, Komatsu Y. Stacked photoelectric conversion device. United States patent 2004, 6825408; November 30.
[68] Higashikawa M, Shimizu T, Honda S, Ishikawa Y, Sano Y. Stack-type photovoltaic element and method of manufacturing stack-type photovoltaic element. United States patent application publication 2012, 2012/0138134; June 7.
[69] Higashikawa M, Shimizu T, Honda S, Ishikawa Y, Sano Y. Stacked photovoltaic element and method of manufacturing stacked photovoltaic element. United States patent application publication 2012, 2012/0125406; May 24.
[70] Nasuno Y, Kohama N, Nakano T. Stacked photoelectric conversion device and method for producing the same. United States patent 2012, 8258596; September 4.
[71] Tachibana S, Sannomiya H. Solar battery cell and for manufacturing method thereof. United States patent 2005, 6870088; March 22.
[72] Jung S-J. Thin film solar cell. United States patent application publication 2011, 2011/0067756; March 24.
[73] Jung S-J, Nam Y-H, Jeon K-W. Photoelectric conversion device. United States patent application publication 2012, 2012/0280232; November 8.
[74] Lim M-H, Park B-H. Thin film solar cell and method of manufacturing the same. United States patent application publication 2011, 2011/0011448; January 20.
[75] Jung S-J. Solar cell and method of fabricating the same. United States patent application publication 2011, 2011/0023954; February 3.
[76] Park J-H, Shin M-H. Solar cell module and method for manufacturing the same. United States patent application publication 2012, 2012/0060890; March 15.
[77] Lee J-E, Kang K-H. Solar cell having reduced leakage current and method of manufacturing the same. United States patent application publication 2011, 0284056; November 24.
[78] Nam Y-H, Kim D-J, Lee J-E, Kang K-H. Photovoltaic module and method of manufacturing the same. United States patent application publication 2012, 2012/0000506; January 5.

[79] Meguro T, Ichikawa M, Sezaki F, Yoshikawa K, Kuchiyama T, Yamamoto K. Thin-film photoelectric conversion device. United States patent application publication 2010, 2010/0243058; September 30.
[80] Sasaki T, Koi Y, Yamamoto K, Yoshimi M, Ichikawa M. Stacked photoelectric converter. United States patent 2009, 7550665; June 23.
[81] Sawada T, Tawada Y, Suezaki T, Yamamoto K. Stack-type photoelectric conversion device. United States patent 2010, 7851695, December 14.
[82] Suezaki T, Yamamoto K. Thin-film photoelectric converter. United States patent application publication 2009, 2009/0014066; January 15.
[83] Yoshikawa K, Ichikawa M, Yamamoto K. Thin film solar cell module. United States patent application publication 2011, 2011/0315190; December 29.
[84] Hayashi K, Tawada Y, Meguro T, Nakajima A. Photovoltaic module. United States Patent 2003, 6632993; October 14.
[85] Hwang S, Ahn S, Lee S. Thin film solar cell. United States patent application publication 2011, 2011/0139232; June 16.
[86] Eo Y-J, Kim B-S, Lee H-M, Lee H-S, Ahn S-W. Thin-film type solar cell and manufacturing method thereof. United States patent application publication 2009, 2009/0178710; July 16.
[87] Son J, Lee H, Ahn J, Yang B, Lee S, Eo Y. Thin film solar cell module and fabricating method thereof. United States patent application publication 2012, 2012/0048330; March 1.
[88] Shim H, Lee S, You D, Lee H, Hwang S, Ahn S, et al. Thin film solar cell. United States patent 2012, 8222517; July 17.
[89] Tanner D, Le H-MH, Gu Q, Sheng S, Chae YK, Su T-F, et al. Method of manufacturing thin film solar cells having a high conversion efficiency. United States patent 2012, 8252624; August 28.
[90] Klein S, Stolley T, Buschbaum S, Rohde M, Schwanitz K, Stoemmer C. Thin-film solar fabrication process, deposition method for solar cell precursor layer stack, and solar precursor layer stack. United States patent application publication 2012, 2012/0080081; April 5.
[91] Sheng S, Chae YK. Microcrystalline silicon alloys for thin film and wafer based solar cell applications. United States patent application publication 2010, 0269896; October 28.
[92] Domine D, Cuony P, Bailat J. Multiple-junction photoelectric device. United States patent 2013, 8368122; February 5.
[93] Soderstrom T, Haug F-J, Niquille X. Multiple-junction photoelectric device and its production process. United States Patent Application Publication 2011, 2011/0226319; September 22.
[94] Ballif C, Haug F-J, Sweetnam S, Söderstrom T. Solar cell and its production process. United States patent application publication 2012, 2012/0186642; July 26.
[95] Kanamoto K, Konishi H, Tokioka H, Yamamuka M, Fuchigami H. Photoelectric converter and manufacturing method thereof, and photoelectric conversion module. United States patent 2013, 8546682; October 1.
[96] Yamamuka M, Orita T, Yamarin H. Thin film solar cell device and method of manufacturing the same. United States patent application publication 2011, 2011/02280189; September 15.
[97] Nishikawa Y, Yashiki Y. Thin film solar cell module and manufacturing method thereof. United States patent application publication 2012, 2012/0318326; December 20.
[98] Bi C-C, Lu C-H. Thin film solar cell and manufacturing method thereof. United States patent 2013, 8445310; May 21.
[99] Lu C-H, Bi C-C. Stacked-layered thin film solar cell and manufacturing method thereof. United States patent 2013, 8552287; October 8.
[100] Bi C-C, Lai K-C. Thin film solar cell. United States patent application publication 2011, 2011/0214722; September 8.
[101] Meier J, Benagli S, Bailat J, Borrello D, Steinhauser J, Hotzel J, et al. Large-area thin-film-silicon photovoltaic modules. United States patent application publication 2011, 2011/0240107; October 6.
[102] Bailat J, Lucle C. Thin-film silicon tandem cell. United States patent application publication 2011, 2011/0259410; October 27.
[103] Bailat J, Koch KW III, Kohnke GE, Marjanovic S, Meier J. Thin film silicon cell in tandem junction configuration on textured glass. United States patent application publication 2013, 2013/0340817; December 26.
[104] Okada N. Stacked photovoltaic element. United States patent application publication 2003, 2003/0217769; November 27.
[105] Tsai C-Y. Thin film solar cell and manufacturing method thereof. United States patent application publication 2011, 2011/0203652; April 25.
[106] Tsai H-C, Lee C-L, Lin Y-T, Tsai Y-M. Multi-bandgap solar cell and method producing the same. United States patent application publication 2011, 2011/0155230; June 30.
[107] Fäy S, Kroll U, Bucher C, Vallat-Sauvain E, Shah A. Low pressure chemical vapour deposition of ZnO layers for thin-film solar cells: temperature-induced morphological changes. Sol Energy Mater Sol Cells 2005;86:385–97.
[108] Fäy S, Feitknecht L, Schlüchter R, Kroll U, Vallat-Sauvain E, Shah A. Rough ZnO layers by LP-CVD process and their effect in improving performances of amorphous and microcrystalline silicon solar cells. Sol Energy Mater Sol Cells 2006;90:2960–7.
[109] Myong SY, Steinhauser J, Schlüchter R, Faÿ S, Vallat-Sauvain E, Shah A, et al. Temperature dependence of the conductivity in large-grained boron-doped ZnO films. Sol Energy Mater Sol Cells 2007;91:1269–74.
[110] Myong SY, Lim KS. Highly stable and textured hydrogenated ZnO thin films. Appl Phys Lett 2003;82:3026–9.
[111] Yao F-Y, Chen S-P, Shing T-K. Solar cell. United States patent application publication 2008, 2008/0236661; October 2.
[112] Coakley K, Stimson B, Rosenthal S, Stephens J, Hussen G, Gurotra K. Photovoltaic modules and methods for manufacturing photovoltaic modules having tandem semiconductor layer stacks. United States patent application publication 2013, 2013/0295710; November 7.
[113] Watai M, Saito K, Komatsu T, Ide Y, Asari S, Mizuno Y, et al. Solar cell. United States patent application publication 2011, 2011/0030780; February 10.
[114] Yan B, Guha S, Yang C. Tandem photovoltaic device with dual function semiconductor layer. United States patent application publication 2011, 2011/0220177; September 15.
[115] Fang H-Y, Kuo C-H, Huang C-F. Solar cell having reflective structure. United States patent application publication 2010, 2010/0126579; May 27.
[116] Fowles GR. Introduction to modern optics. 2nd ed.. New York: Holt, Rinehart and Winston, Inc.; 1975; 96–102.
[117] Myong SY. Current status of inorganic solar cells using quantum structures. Recent Pat Nanotechnol 2012;6:2–9.
[118] Moulin E, Sukmanowski J, Schulte M, Gordijn A, Royer FX, Stiebig H. Thin Solid Films 2008;516:6813–7.
[119] Eminian C, Haug FJ, Cubero O, Niquille X, Ballif C. Photocurrent enhancement in thin film amorphous silicon solar cells with silver nanoparticles. Prog Photovolt: Res Appl 2011;19:260–5.
[120] Atwater HA, Polman A. Plasmonics for improved photovoltaic devices. Nat Mater 2010;9:205–13.
[121] Schaadt DM, Feng B, Yu ET. Enhanced semiconductor optical absorption via surface plasmon excitation in metal nanoparticles. Appl Phys Lett 2005;86 (Article ID 063106. 3 pp.).
[122] Haug FJ, Soderstrom T, Cubero O, Terrazzoni-Daudrix V, Ballif C. Plasmonic absorption in textured silver back reflectors of thin film solar cells. J Appl Phys 2008;104 (Article ID 064509. 7 pp.).
[123] Arai M, Yamasaki K, Ogawa S, Hayashi T. Transparent electroconductive film for solar cell, composition for transparent electroconductive film and multi-junction solar cell. United States patent application publication 2011, 2011/0139228; June 16.
[124] Arai M, Yamasaki K, Ogawa S, Hayashi T. Transparent electroconductive film for solar cell, composition for transparent electroconductive film and multi-junction solar cell. United States patent application publication 2014, 2014/0090699; April 3.
[125] Murata M. Integrated tandem-type thin film solar cell module and method for manufacturing the same. United States patent application publication 2011, 2011/0041889; February 24.
[126] Jung S-J, Kim B-J, Shin M. Low-refractive-index and high-transmittance silicon oxide with a mixed phase of n-type microcrystalline silicon as intermediate reflector layers for tandem solar cells. Sol Energy Mater Sol Cells 2014;121:1–7.
[127] Mercaldo LV, Veneri PD, Usatii I, Esposito EM, Nicotra G. Properties of mixed phase n-doped silicon oxide layers and application in micromorph solar cells. Sol Energy Mater Sol Cells 2013;119:67–72.
[128] Myong SY, Jeon LS. Improved light trapping in thin-film silicon solar cells via alternated n-type silicon oxide reflectors. Sol Energy Mater Sol Cells 2013;119:77–83.
[129] Boccard M, Battaglia C, Blodiaux N, Pugin R, Despeisse M, Ballif C. Smoothing intermediate reflecting layer for tandem thin-film silicon solar cells. Sol Energy Mater Sol Cells 2013;119:12–7.
[130] Bielaway A, Üpping J, Miclea PT, Wehrspohn RB, Rockstuhl C, Ledere F, et al. 3D photonic crystal intermediate reflector for micromorph thin-film tandem solar cell. Phys Status Solidi A 2008;205:2796–810.
[131] Bielaway A, Rockstuhl C, Ledere F, Wehrspohn RB. Intermediate reflectors for enhanced top cell performance in photovoltaic thin-film tandem cells. Opt Express 2009;17:8439–46.
[132] O'Brien PG, Chutinan A, Leong K, Kherani NP, Ozin GA, Zukotynski S. Photonic crystal intermediate reflector for micromorph solar cells: a comparative study. Opt Express 2010;18:4478–90.
[133] Söderström T, Haug F-J, Niquille X, Terrazzoni V, Ballif C. Asymmetric intermediate reflector for tandem micromorph thin film silicon solar cells. Appl Phys Lett 2009;94 (Article ID 063501. 3 pp.).
[134] Hwang S-T, You DJ, Kim SH, Lee S, Lee H-M. Large area Si thin film solar module applying n-μc-$SiO_x$:H intermediate layer with low refractive index. Sol Energy Mater Sol Cells 2013;113:79–84.
[135] Kim S, Chung J-W, Lee H, Park J, Heo Y, Lee H-M. Remarkable progress in thin-film silicon solar cells using high-efficiency triple-junction technology. Sol Energy Mater Sol Cells 2013;119:26–35.
[136] Yan B, You G, Sivec L, Yang J, Guha S, Jiang C-S. Innovative dual function nc-$SiO_x$:H layer leading to a $>16\%$ efficient multi-junction thin-film silicon solar cell. Appl Phys Lett 2011;99 (Article ID 113512. 3 pp.).
[137] Guha S, Yang J, Yan B. High efficiency multi-junction thin film silicon cells incorporating nanocrystalline silicon. Sol Energy Mater Sol Cells 2013;119: 1–11.